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WASTEWATER DEMINERALIZATION BY CONTINUOUS COUNTER-CURRENT ION EXCHANGE PROCESS

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Office of Research and Development
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16 ABSTRACT

A wastewater demineralization study employing a 38 l pm (10 gpm) continuous counter-current ion exchange pilot plant, manufactured by the Chemical Separations Corporation, Oak Ridge, Tennessee, has been conducted at the County Sanitation Districts, Pomona Research Facility, Pomona, California. Under steady state conditions TDS removal of 82% was achieved with a feed TDS of 500-600 mg/l. Monovalent cation leakage resulting from inadayne rinse reduced TDS removal below that obtained with a 2-stage fixed bed process tested at the same site.

The continuous counter-current ion exchange pilot plant has demonstrated a promising regeneration efficiency for both cation and anion exchangers. The brine volume produced by the process was approximately 8 percent of the product flow, thus yielding a 92 percent water recovery. The annual resin operation losses were about 5 percent for the cation exchanger and 15 percent for the anion exchanger. These high resin losses, however, account for less than 5 percent of the total process cost.

A cost estimate for a 37,850 cu m/day (10 MGD) continuous counter-current ion exchange plant based on Pomona pilot plant operating results has been made. The estimated total process cost of 4.8¢/1000 gallons) was based on the use of carbon treated secondary effluent with an average TDS concentration of 600 mg/l to produce a product water with 82 percent reduction in TDS.

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

Renovation of wastewater for recycle and reuse may require partial demineralization of effluents from convention treatment. This report summarizes studies of demineralization of secondary effluent by a unique ion exchange process. The technique employed provides continuous counter-current contact between the wastewater and the ion exchange resins which provides potential economies over the conventional contacting techniques.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

A wastewater demineralization study employing a 38 lpm (10 gpm) continuous counter-current ion exchange pilot plant, manufactured by the Chemical Separations Corporation, Oak Ridge, Tennessee, has been conducted at the County Sanitation Districts' Pomona Research Facility, Pomona, California. The study was jointly funded by the U.S. Environmental Protection Agency and the County Sanitation Districts of Los Angeles County.

The continuous counter-current ion exchange pilot plant has demonstrated a promising regeneration efficiency for both cation and anion exchangers. The brine volume produced by the process was approximately 8 percent of the product flow, thus yielding a 92 percent water recovery. The annual resin operation losses were about 5 percent for the cation exchanger and 15 percent for the anion exchanger. These high resin losses, however, account for less than 5 percent of the total process cost.

A cost estimate for a 37,850 cu m/day (10 MGD) continuous counter-current ion exchange plant based on Pomona pilot plant operating results has been made. The estimated total process cost of 4.8¢/1,000 liters (18.3¢/1,000 gallons) was based on the use of carbon-treated secondary effluent with an average TDS concentration of 600 mg/l to produce a product water with 82 percent reduction in TDS.

This report was submitted by County Sanitation Districts of Los Angeles County in fulfillment of Contract No. 14-12-150 under the partial sponsorship of the U.S. Environmental Protection Agency. Work on this report was completed as of August 1972.

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Great appreciation is also extended to the operating and laboratory staff of the Pomona Advanced Wastewater Treatment Research Facility.

SECTION 1

INTRODUCTION

An extensive wastewater demineralization study has been conducted since 1967 at the County Sanitation Districts' Pomona Research Facility, which is totally funded by the U.S. Environmental Protection Agency and the County Sanitation Districts of Los Angeles County. The study has covered the reverse osmosis, electrodialysis and ion exchange processes. The preliminary results of this extensive study indicated that the ion exchange process was most promising for wastewater demineralization based on both economical and technical considerations(1). The ion exchange pilot plant employed in previous wastewater demineralization studies was a conventional fixed-bed system(2). Recently some moving-bed ion exchange systems which have been shown to be more efficient than the fixed-bed system in both municipal and industrial water treatments are available on the market. Therefore, the wastewater demineralization study has been expanded to include the moving-bed ion exchange process. The results of this special study are presented in this report.

A continuous (moving-bed) counter-current ion exchange process has the following inherent advantages and disadvantages as compared with the conventional fixed-bed ion exchange process.

A. Advantages:

1. A smaller resin inventory is required.

2. Resin regeneraton is more efficient.

3. Ion leakage is lower at a given level of regenerant.

4. Brine disposal problem is minimized.

B. Disadvantages:

1. More sensitive and accurate automation system for efficient process control is required.

2. Higher operating pressure is required.

3. Resin attrition loss is greater.

This study has been conducted to determine if the advantages outweigh the disadvantages for the demineralization of wastewater. More specifically, the objectives of this study are: (a) to optimize the operating parameters of a continuous counter-current ion exchange system for wastewater demineralization; and (b) to develop the process cost for wastewater demineralization by the continuous counter current ion exchange system.

Because of the dynamic nature of the system operation, it requires a great deal of balancing and adjustment in a continuous counter-current ion exchange process to achieve an optimum performance. Therefore, a high degree of flexibility and accuracy in the various functional controls is very essential for a successful process demonstration. Unfortunately, the continuous counter-current ion exchange pilot plant provided by the Chemical Separations Corporation (Chem-Seps) of Oak Ridge, Tennessee, was not well equipped with such necessary features in its original design. Consequently, a series of major corrections and modifications had been done on the pilot plant before a six month period of intensive process evaluation study was satisfactorily initiated in March, 1972.

SECTION 2

CONCLUSIONS

The following conclusions can be drawn from this pilot plant study:

A. The continuous counter-current ion exchange process requires a more sophisticated process control system than the conventional fixed-bed co-current ion exchange process. Particularly, an accurate control of the resin pulsing operation is very essential for the success of the process.

B. The continuous counter-current ion exchange process achieved an 88 percent regeneration efficiency for the cation exchanger and 90 percent efficiency for the anion exchanger, which were slightly better than those obtained for a two-stage fixed-bed ion exchange process operating on the same wastewater with same levels of regenerant dosages.

C. The monovalent ion removal achieved by the continuous ion exchange system in this study was poorer than the fixed-bed ion exchange system in the previous study.

D. The brine volume produced by the continuous counter-current ion exchange process was about 8 percent of the product flow, thus yielding a 92 percent water recovery.

E. The actual resin losses caused by the plant operation were estimated to be about 1.5 percent for the cation exchange resin and 4.5 percent for the anion exchange resin during the 2,760 hours of on-stream operation.

F. The cost for the process to achieve a 82 percent TDS reduction from a 600 mg/l TDS feed water in a 37,850 cum/day (10 MGD) plant is estimated to be 4.8¢/1,000 liters (18.3¢/1,000 gallons) of product water. The costs for the carbon adsorption pretreatment and the brine disposal are not included in the process cost estimate.

G. The total process cost, including the carbon adsorption pretreatment, for a blended product water with 500 mg/l TDS is about 3.3¢/1,000 liters (12.8¢/1,000 gallons).

SECTION 9

RECOMMENDATIONS

Although some shortcomings pertaining to the mechanical design of the Chem-Seps pilot plant have prevented the studies from being completely successful, these studies have revealed some promising results. These results have well justified pursuing a research effort on the continuous counter-current ion exchange process for wastewater demineralization.

The following objectives are proposed to be achieved by the future pilot plant studies:

A. To fully demonstrate the capability of the continuous counter-current ion exchange process in controlling the leakage of the monovalent ions;

B. To devise some effective means of rinse control to prevent the undesirable contamination of the product water by the excessive regenerants;

C. To overcome the problems associated with the lime slurry application;

D. To demonstrate the long-term reliability of the process performance;

E. To study the effects of the high TDS feed water upon the process performance and process economy;

F. To study the attrition effects of the process operation upon the resin life on a long-term operation basis; and

G. To study the feasibility of recovering the ammonium ion from the brine, in the form of the valuable ammonium nitrate, by adopting a new HNO_3-NH_4OH regeneration scheme.

SECTION 4

PROCESS AND PILOT PLANT DESCRIPTIONS

PROCESS FEATURES

The basic ion exchange reactions involved in an ion exchange process are practically the same for the fixed-bed co-current and the continuous counter-current ion exchange systems. However, the reaction rate and process efficiency are somewhat different between the two systems. The continuous counter-current ion exchange system may be more efficient due to the special features employed in its system design. These special features and their functions are described as follows:

A. The system can simultaneously perform the four basic operating cycles - demineralization, backwash, regeneration and rinse - in a single loop column separated by control valves. This multiple operation function greatly reduces the necessary resin inventory and thus the capital cost.

B. The flow of the regenerated resin is opposite to the flow of the feed water, which is in a downflow pattern. This counter-current flow feature insures that the last resin the feed water being contacted with is in the freshest stage of regeneration, thus making effective the removal of the monovalent ions which are at the lower end of the selectivity list, such as sodium, potassium, ammonium, chloride and nitrate ions.

C. The regenerant flow is counter to the flow of the exhausted resin. The exhausted resin is introduced into the regeneration section from the outlet end of the regenerant waste. Therefore, the resin can be progressively regenerated by stronger regenerant as it flows further through the regeneration section. This flow pattern can achieve the following objectives:

1. Minimizing the formation of calcium sulfate precipitates in the resin bed when sulfuric acid is employed as regenerant for cation exchanger.

2. Minimizing the handling problem when the low cost lime slurry is used as the regenerant for anion exchanger.

3. Maximizing the utilization of regenerant.

6. The continuous flow function of the process allows the brine stream to be more uniform in terms of quantity and quality, thus minimizing the brine disposal problems.

PILOT PLANT DESCRIPTION

General

The Chem-Seps continuous counter-current ion exchange pilot plant contained all the aforementioned features in its design for this study. The pilot plant had a design capacity of 38 liters (10 gallons) of product water per minute. The plant consisted of one cation exchange unit and one anion exchange unit mounted together on a structural steel frame, as shown in Figure 1. The units were of identical design, except for some minor additions for the slurry handling in the anion unit. Each unit consisted basically of a loop made up of five functional sections (treatment, backwash, pulse, regeneration, and rinse sections) in four vessels (loading, overflow, pulse, and regeneration vessels) as shown in Figure 2. The pneumatically operated butterfly valves separated the vessels from one another. All vessels were constructed of 15.2 cm (6 in) diameter fiberglass column, except the loading vessel, which was a 20.3 cm (8 in) diameter fiberglass column.

The resins were transferred hydraulically around the entire loop in the sequence of loading vessel, overflow vessel, pulse vessel,and regeneration vessel. The frequency and quantity of the resin transfer were regulated by a control panel.

Functions of Various Vessels

The specific function of each vessel in the pilot system is summarized as follows:

Loading Vessel (Treatment Section)

The minerals in the form of cations and anions were removed from the feed water in this vessel. The feed water entered the vessel through distributor and left through collector. The distributor and collector were designed to provide equal distribution and collection of water over the cross-section of the vessel. The distributor was a slot-opening type of design without a screen, while the collector was provided with Johnson well screen (approximately 0.4 mm opening) to prevent resin from entering the product water.

Overflow Vessel (Backwash Section)

This vessel received the exhausted resin from the loading vessel during the pulse period. The pulse water flowed out of the top of this vessel, as indicated in Figure 2.

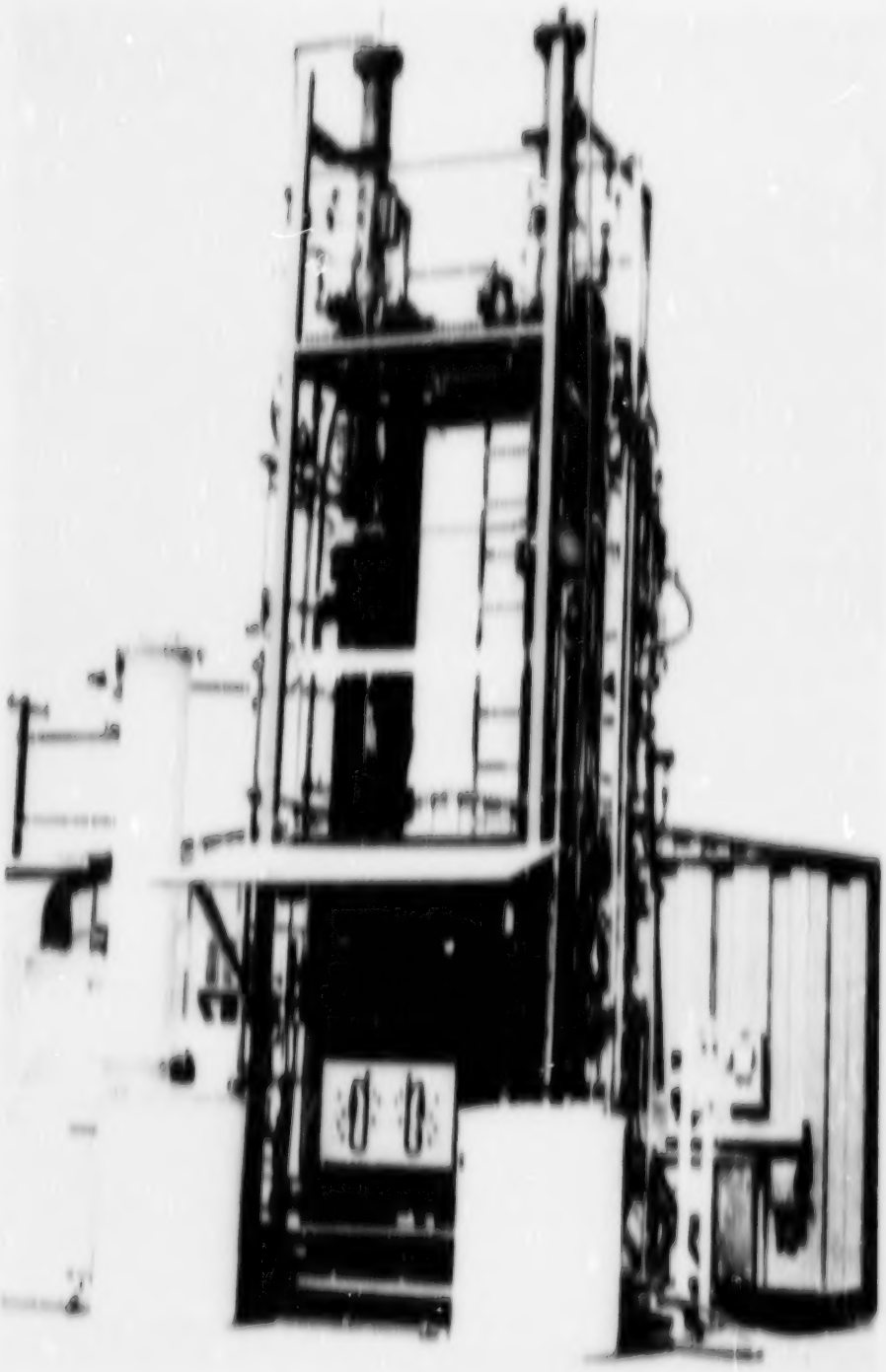
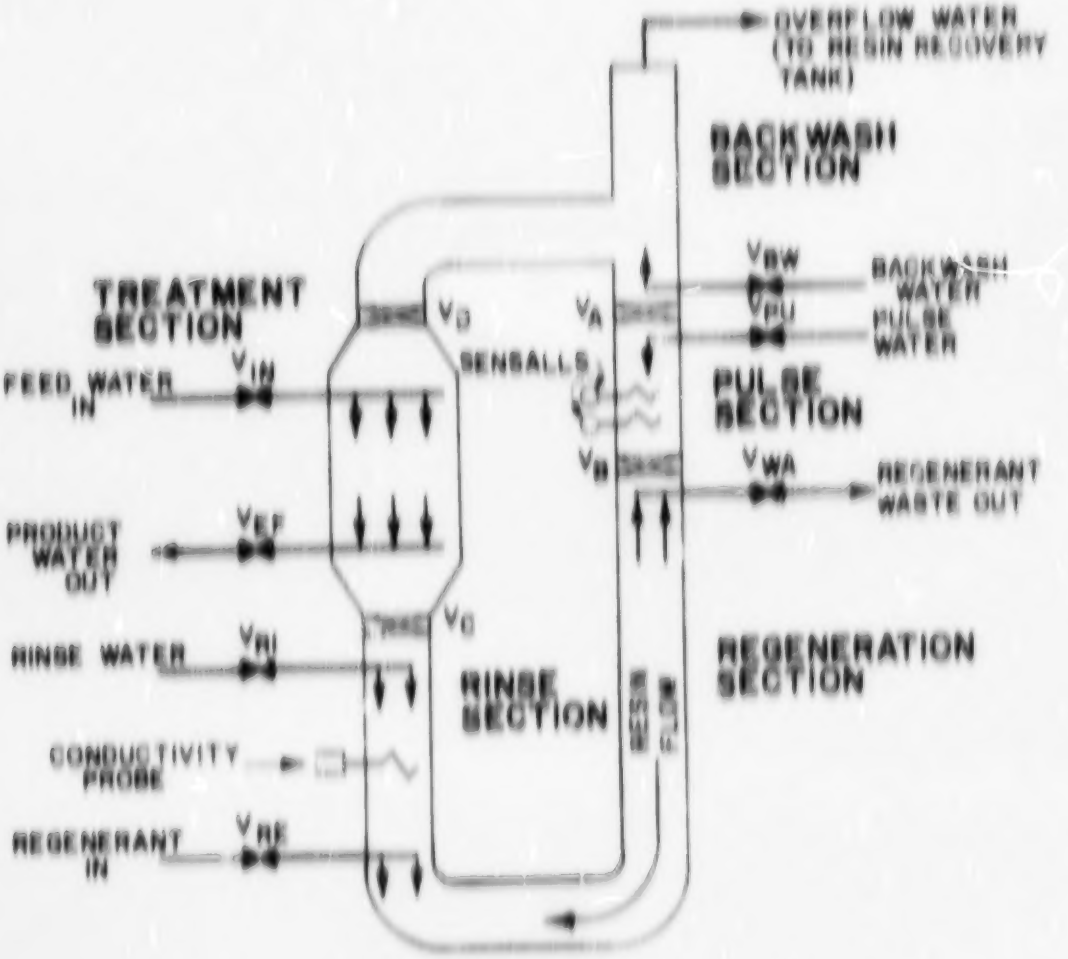


Figure 1. Photograph of CHEM-SEPS continuous counter-current ion exchange pilot plant.



VALVE POSITIONS DURING CYCLES

RUN CYCLE		PULSE CYCLE	
VALVES OPEN	VALVES CLOSED	VALVES OPEN	VALVES CLOSED
A, WA, IN, EF, AND RE.	B, C, D AND PU.	B, C, D AND PU.	A, WA, IN, EF, AND RE.

Figure 2. Schematic diagram of CHEM-SEP'S continuous counter-current ion exchange contactor.

During the normal operation period other than the pulse period, the backwash water entered this vessel and washed the suspended solids and resin fines out of this vessel into the resin recovery tank. The resin fines consisted of small resin particles produced by mechanical attrition or osmotic shock.

A sight glass was installed in this vessel to allow visual examination of the resin level. A proper resin level was maintained in the vessel to insure that a sufficient amount of resin was in the unit for effective and accurate operation.

Pulse Vessel (Pulse Section)

The major function of this vessel was to initiate and control the movement of resin around the loop from one vessel to the other. The cleaned but exhausted resin from the overflow vessel was transferred to this vessel by gravity. The exact amount of resin to be transferred was controlled by the upper-limit ultra sonic sensor (Sensall), which sent out a signal to close the valve as soon as the resin had reached the pre-set level.

During the pulse period, high pressure water entered this vessel and pushed the resin out of the vessel into the regeneration vessel. The amount of resin movement was closely controlled by the lower-limit ultra sonic sensor. The distance between the two sensors could be adjusted to provide the proper amount of resin movement per pulse period. The actual resin movement could be measured by means of the sight glass provided in the vessel. A pulse timer was used as a backup for the Sensall pulse control.

Regeneration Vessel (Regeneration and Rinse Sections)

In this vessel an appropriate amount of regenerant was used to regenerate the exhausted resin, and the regenerated resin was then rinsed free of excess regenerant before being pulsed into the loading vessel. Teflon-coated Johnson well screens were used to prevent the resin from entering the regenerant distributor and regenerant waste collector. The waste collector screen could be replaced easily when it became clogged by chemical precipitate.

The product water was used as rinse water which entered through the distributor and passed through the resin bed to displace the excess regenerant. The rinse water was automatically controlled by a conductivity probe inside the rinse section. A flow meter was used to indicate the flow rate of rinse water so that a proper flow rate could be maintained to prevent any channeling through the resin bed.

Resin Characteristics

Basically, the Chem-Seps continuous counter-current ion exchange pilot plant was a modified combination system of a strong acid cation exchanger and a weak base anion exchanger. The cation column employed a mixture of strong and weak acid cation exchange resins, instead of strong acid cation exchange resin alone. By utilizing such a mixture of strong and weak acid type resins, the excess acid, which was required for an efficient regeneration of the strong acid resin, could be utilized for regeneration of the weak acid resin because of its higher proton affinity. The proper fractional amount of the weak acid cation exchange resin in such a resin mixture was determined by the characteristics of the feed water quality, more specifically, the fractional amount of the bicarbonate ions in the water to be treated. A combination of 50 percent strong and 50 percent weak acid cation exchange resin mixture was recommended by Chem-Seps for Pomona wastewater demineralization study.

The resins selected for this study were Duolite C-20 strong acid cation resin, Duolite CC-3 weak acid cation resin and Duolite ES-340 weak base anion resin. All these resins were manufactured and supplied by Diamond Shamrock Chemical Company, Redwood City, California. Some of the major physical and chemical characteristics of the resins are shown in Table I.

The cation resin mixture was regenerated with 2.5 percent sulfuric acid solution, while the anion resin was regenerated with either 1.5 percent calcium hydroxide solution (hydrated lime slurry) or 4 percent ammonium hydroxide solution.

TABLE 1. RESIN PROPERTIES AND CHARACTERISTICS (3)

Parameter	Duolite C-20	Duolite CC-3	Duolite ES-340
Resin Composition	Styrene-DVB	Crosslinked Polyacrylic Acid	Epoxy-Amine
Functional Groups	Sulfonic Acid	Carboxylic Acid	Tertiary Amine
Ionic Form	Hydrogen (H)	Hydrogen (H)	Free Base (DM)
Physical Form	Reddish-Brown Translucent Beads	Amber-Colored Translucent Beads	Pale-Gold Translucent Beads
Specific Gravity	1.32 (Na Form)	1.32 (Na Form)	1.5± (Cl Form)
Moisture Content	43.46± (Na Form)	48-53± (H Form)	56-62± (Cl Form)
Particle Size (Typical)			
U.S. Standard Sieve	16-50 Mesh	16-50 Mesh	16-50 Mesh
Effective Size	0.53 mm	0.42-0.54 mm	
Uniformity Coefficient	1.49	1.6 Maximum	
Total Exchange Capacity:	2.1 meq/ml	4.2 meq/ml	3.0 meq/ml (to H_2SO_4)[3] 2.6 meq/ml (to HCl)[4]

SECTION 5

PILOT PLANT OPERATION

GENERAL

The installation of the Chem-Seps continuous counter-current ion exchange pilot plant was completed in July, 1971 at Romona Research facility. The initial start up of the pilot plant operation was scheduled on August 2, 1971. However, successful pilot plant operation was not achieved until March 1, 1972. During the unsuccessful trial run period, a series of major system alterations and modifications were made on the pilot plant to provide the necessary control mechanisms for the process study.

The pilot plant was operated satisfactorily using H_2SO_4 - NH_4OH mode of regeneration during the first half of March, 1972. The operation was then converted to the H_2SO_4 - $Ca(OH)_2$ (lime slurry) regeneration mode. An air stripping tower was installed between the cation and anion units, as illustrated in Figure 3. The CO_2 was stripped from the effluent of the cation unit to prevent the formation of $CaCO_3$ precipitate inside the anion unit. This operation mode was continued through the first week of May, 1972. However, the operational results, which will be discussed in Section 6, indicated that the existing pilot plant system was not able to utilize lime slurry successfully for regeneration. Consequently, the attempt to achieve the utilization of the low cost lime slurry for the regeneration of the weak base anion exchange resin was abandoned.

On May 16, 1972, the pilot plant operation reverted to the H_2SO_4 - NH_4OH regeneration mode. The air stripping tower was bypassed for this mode of operation. The pilot plant was operated continuously from 8:00 a.m. on Monday through 4:00 p.m. on Friday every week throughout most of the investigation period. The operation of the Chem-Seps continuous counter-current ion exchange pilot plant was terminated on August 31, 1972, after the expiration of the six-month minimum rental period of the pilot plant.

OPERATING CONDITIONS

Some of the important operating conditions employed for the pilot plant operation are described in the following under each specific process function.

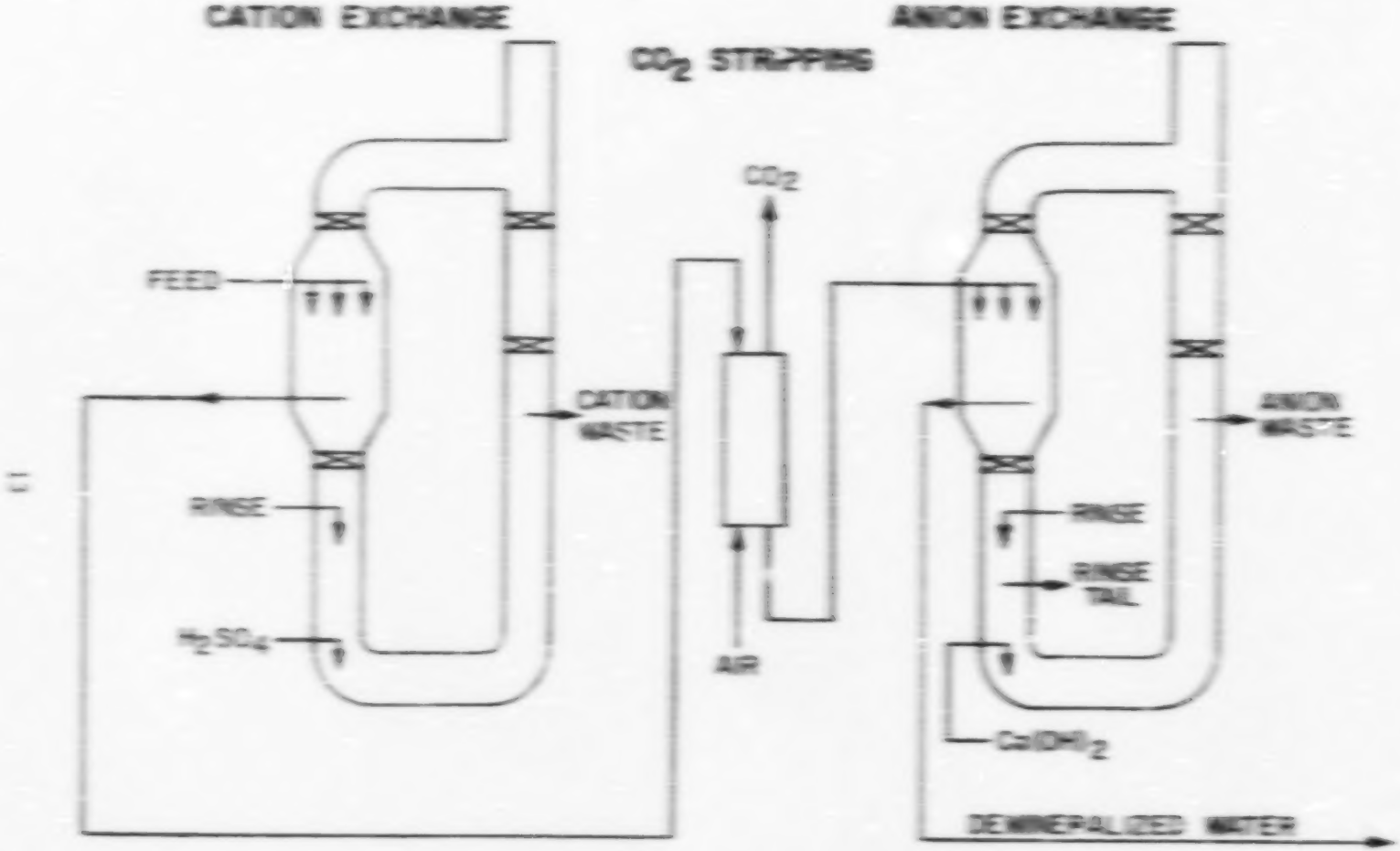


Figure 3. General layout of the CHEM-SEPS continuous counter-current ion exchange pilot plant.

Demineralization

The demineralization process was accomplished by the treatment sections of both cation and anion units. Each treatment section contained about 80 liters of resin between the inlet and outlet levels, thus providing about one minute of empty-bed detention time for a normal 78 lpm feed water flow. The hydraulic loading in both treatment sections under the same 38 lpm flow was about 17.3 l/sec/sq m (25.5 gpm/sq ft). The feed pressure was regulated at 3.5 kg/sq cm (50 psi) for the cation unit and the residual pressure in the product water for the anion unit was around 0.7 kg/sq cm (10 psi).

Two intermediate sampling points, F-1 and F-2, were provided in each treatment section as shown in Figure 4. Samples could be taken from these points to evaluate the degree of the resin exhaustion. Every 10 minute period the demineralization cycle was interrupted by the resin pulsing operation. About 10 percent of the resin in each treatment section was replaced by the freshly regenerated resin for every pulse cycle. The exhausted resin was pulsed into the backwash section for backwash process.

Backwash

Carbon-treated secondary effluent water, which was the feed water for the pilot system, was employed as the backwash water. The backwash flow rate was controlled by a throttle valve and was indicated by the backwash flow meter. The flow rate was set at 3.6 l/sec/sq m (5.2 gpm/sq ft) for both cation and anion exchange resins. At this flow rate, the resin bed expansion was expected to be in the range of 50 percent to 100 percent, depending on the actual process temperature and resin type. Sufficient amount of freeboard was provided in each overflow vessel to accommodate the expected bed expansion.

The duration of backwash cycle was controlled by the same programmer as the demineralization cycle, which was set for 10 minutes for each cycle. However, the 10 minute duration seemed too long for the pilot plant backwash operation. A second control timer could be installed to reduce the duration of the backwash cycle to save the backwash operation cost, but it was not done in this study.

The suspended solids, resin fines and, possibly, some perfect resin beads in the backwash wastes of the cation and anion units were collected respectively in the cation and anion resin recovery tanks. Most of the perfect resin beads could be recovered from each resin recovery tank by flotation separation method. Both suspended solids and resin fines should be washed out of the cation and anion units to prevent plugging of the collector screens and the resin beds.

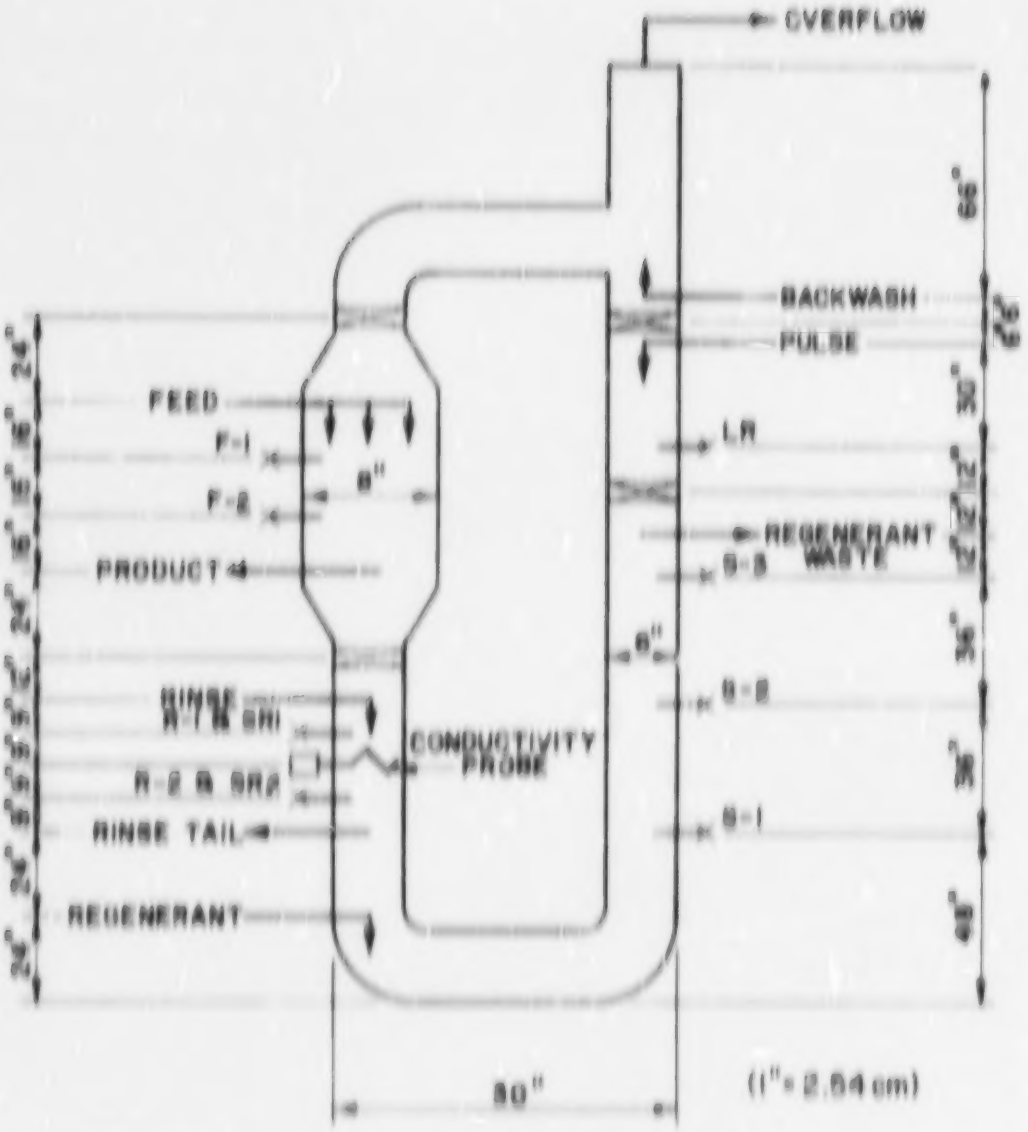


Figure 4. Layout of pilot plant sample points.

Pulse

The purpose of pulsing the resin is to move exhausted resin out of the treatment section and replace it with regenerated resin. Since the accuracy of the resin movement will directly affect the pilot plant performance, the assurance of the precision and reliability of the control mechanisms in the pulsing operation is overwhelmingly important.

In the Chem-Seps pilot plant, the amount of resin movement for every pulse cycle was controlled by two ultra sonic sensors in each pulse section. The total resin movement was regulated at 20.3 cm (8 in) per pulse cycle for both cation and anion units, which was equivalent to about 3.7 liters (0.13 cu ft) of resin per pulse. The rate of pulsing the resin was maintained in the range of 2.5 to 5.1 cm (1 to 2 in) per second and was controlled by a manual throttling valve. The carbon-treated secondary effluent pressurized at approximately 4.4 kg/sq cm (63 psi) was used as pulsing water. The volume of water required to move the resin in every pulse cycle was practically equal to the volume of the resin transferred.

The pulsing operation of the pilot plant was programmed to be carried out one unit at a time, starting with the cation unit first and then the anion unit. It usually took 10 to 15 seconds for the cation unit to build up pressure to initiate the pulsing and about 5 seconds to complete the resin transfer, while it took from 20 to 40 seconds for the anion unit to initiate the pulsing and about 5 to 8 seconds to complete the resin transfer. Therefore, the total pulsing time ranged from 40 seconds to 60 seconds.

During the pulsing cycle, all other process functions (demineralization, backwash, regeneration and rinse) were temporarily suspended, and they resumed operations simultaneously as soon as the pulsing operation was completed.

Regeneration

Cation Exchange Resin

The regeneration of the cation exchange resin was accomplished by the sulfuric acid at a feed concentration of 2.5 percent. A 4 percent sulfuric acid solution which was employed in the previous study of a fixed-bed ion exchange system (2) was found to cause serious plugging of the waste collector screen in this study.

The flow of the 2.5 percent sulfuric acid was maintained continuously through every ten minute run cycle at a rate of approximately 38 liters (10 gallons) per hour. At this normal flow rate, the actual detention time for the sulfuric acid in

the regeneration section ranged from 20 minutes to 60 minutes, depending on the rinse water flow conditions. The flow rate of the regenerant was controlled and regulated by a throttling valve and a flow indicator on the regenerant feed line.

The average feed pressure for the regenerant flow was about 1.0 kg/sq cm (15 psi) at the normal flow rate of 38 liters (10 gallons) per hour. However, the feed pressure was found to vary from 0.6 to 1.4 kg/sq cm (8 to 20 psi) from one run cycle to another, depending on the conditions of the packing of the resin bed and the plugging of the waste collector screen inside the regeneration section. This feed pressure variation caused substantial rate fluctuation for the regenerant flow.

Anion Exchange Resin

During the study period with the H_2SO_4-$Ca(OH)_2$ regeneration mode, a 1.5 percent $Ca(OH)_2$ slurry was used as the regenerant for the regeneration of the weak base anion exchange resin. The lime slurry was initially made up from low cost slacked lime. However, it was found that the slacked lime contained some small "chunks," which acted like resin particles and traveled co-currently with the resin into the treatment section, thus degrading the quality of the product water. Consequently, finer quality hydrated lime was used to replace the slacked lime for making up the 1.5 percent $Ca(OH)_2$ slurry after April 3, 1972. The flow rate of the lime slurry was maintained approximately at 23 liters (6 gallons) per hour. At this flow rate, the detention time for the lime slurry in the regeneration section was about 100 minutes, provided the rinse water was effectively discharged through the rinse tail as shown in Figure 3.

The H_2SO_4 -$Ca(OH)_2$ regeneration mode was converted to H_2SO_4-NH_4OH mode after two months of poor performance associated with the lime slurry application. During the H_2SO_4-NH_4OH operation period, the flow rate of the 4 percent NH_4OH was maintained at about 7.6 liters (2 gallons) per hour under an average feed pressure of 1.3 kg/sq cm (18 psi). Unlike the cation unit, the feed pressure for the NH_4OH in the anion unit was quite consistent throughout the entire period of study. The actual detention time for the ammonium hydroxide solution in the regeneration section was estimated to range from 30 minutes to 270 minutes, depending on the rinse water flow conditions.

Rinse

The demineralized water was employed as the rinse water for both cation and anion units. The flow of the rinse water was not continuous through the ten minute run cycle. The actual duration of the rinse water flow was controlled by the conductivity probe installed in each rinse section. The rinse flow was turned off automatically when the conductivity measured by the probe dropped

below the pre-set level. The rinse flow was regulated by a throttling valve and maintained at 7.6 liters (2 gallons) per minute for both cation and anion units.

Since the duration of the rinse flow varied slightly from cycle to cycle, the total volume of rinse water used also varied somewhat. The average amounts of rinse water for cation and anion units during the operation of the H_2SO_4-NH_4OH regeneration mode were equal to 3 and 4 bed volumes of the processed cation and anion exchange resins, respectively.

For the H_2SO_4-$Ca(OH)_2$ regeneration mode, the rinsing condition for the cation unit was similar to the aforementioned one. However, the volume of the rinse water for the anion unit was substantially increased to 12 bed volumes of resin. Therefore, a rinse tail had to be installed in the anion unit to remove this big stream of rinse water to prevent the unfavorable dilution of the regenerant flow.

SAMPLING AND TESTING

During the pilot plant operation period, one-hour composite samples from the various streams of feed, product and brine were taken daily between 7:30 a.m. and 8:30 a.m. for performance evaluation. In addition to this sampling schedule, a conductivity probe was installed in the product line to record the entire sequence of product quality. All samples were analyzed at Pomona Research Laboratory for the concentrations of the major cations and anions, total dissolved solids, total alkalinity, acidity, pH and conductivity.

Besides the daily one-hour composite samples, some grab samples were also frequently taken at various points, as shown in Figure 4. The grab samples taken from the F-1 and F-2 sampling points were used to determine the pH loading profiles of the treatment sections in both cation and anion units. The efficiency of the rinsing operation was evaluated by the samples taken from the R-1 and R-2 sampling points. The resin samples, SR1 and SR2, were used for determining the extent of chemical stripping or state of regeneration, while the degree of resin exhaustion was determined by the ER resin samples. Some grab samples were also taken at the S-1, S-2 and S-3 sampling points for the evaluation of the rate of decreasing strength of the regenerant along the path of the regenerant flow. All these grab samples served to monitor the various process functions and optimize the overall pilot plant performance.

The analytical procedures for the cations and anions were specified in the Standard Methods for the Examination of Water and Wastewater (4), while the exchange capacities of both exhausted and regenerated resins were determined by the simplified

methods as described in Appendix A. The analytical procedures for determining the total salts in the samples of S-1, S-2, S-3 and regenerant waste were presented in Appendix B.

SECTION 6

RESULTS AND DISCUSSIONS

During the first part of the study, the pilot plant operation was interrupted many times, with the shut-down period varying from several days to as much as three months. The interruptions were required to make necessary repairs and modifications of the system control mechanisms. As a result of this on-and-off operation mode, most of the experimental data collected before March, 1972 are not considered significant, and thus they are not included in this report. No major mechanical problem was encountered during the second part of the study from March to August of 1972, which was officially considered as the six month minimum rental contract period for the Chem-Seps pilot plant.

The long delay in the formal start-up of the pilot plant operation has resulted in a cancellation of the long-term study of the continuous counter-current ion exchange process. Therefore, the experimental results and discussions presented in this report are based on the six month short-term study.

REMOVAL OF IONIC IMPURITIES

When the H_2SO_4-$Ca(OH)_2$ regeneration mode was employed, the rinsing of the regenerated resins in the anion unit was never satisfactorily achieved. Both calcium carbonate and calcium sulfate precipitates were transferred into the treatment section with the anion exchange resin during the pulsing operation. These precipitates were slightly dissolved in the water inside the treatment section and caused serious contamination of the product water. The high concentrations of the calcium and sulfate ions in the final product water, as indicated in Table 2, fully demonstrated the contamination effect of the chemical precipitates.

The concentration of the sulfate ion was also frequently found to be higher in the cation column effluent than the feed water during both series of operations using two different regeneration modes. The increase of the sulfate ion in the cation column effluent could result from the dissolution of the calcium sulfate precipitates embedded in the cation exchange resins, or it could result from an inadequate rinsing of the excessive sulfuric acid out of the cation exchange resins. As a result of

TABLE 2. TYPICAL PILOT PLANT PERFORMANCE USING H_2SO_4-$Ca(OH)_2$ REGENERATION MODE

Parameter		Carbon Column Effluent (Feed)	Cation Column Effluent	Anion Column Effluent (Product)	Removal %
Calcium	mg/l	60	1.0	30	53
Magnesium	mg/l	6.7	0.40	1.7	75
Sodium	mg/l	125	23	43	82
Potassium	mg/l	7.3	2.2	2.2	70
Ammonium (NH_4-N)	mg/l	25	4.2	4.3	83
Sulfate	mg/l	72	119	78	
Chloride	mg/l	132	136	44	67
Nitrate (NO_3-N)	mg/l	0.17	0.05	0.05	71
Phosphate (PO_4)	mg/l	29	27	3.7	86
Total Alkalinity ($CaCO_3$)	mg/l	260		28	
Acidity ($CaCO_3$)	mg/l		196		
Total Dissolved Solids	mg/l	543	191	214	61
pH		7.2	2.6	6.3	
Conductivity	micromhos/cm	1140	1660	380	67

this additional loading of the sulfate ion, the removal efficiencies of the chloride and orthophosphate ions were substantially reduced in the anion exchange column. Consequently, the overall removal of the ionic impurities, expressed as TDS removal, during the H_2SO_4-$Ca(OH)_2$ operation series was very poor. The TDS removal was found to vary widely from 10 percent to 70 percent, with an average of 50 percent.

The contamination of the final product water by the calcium sulfate and the calcium carbonate precipitates in the H_2SO_4-$Ca(OH)_2$ mode of operation was eliminated by the use of an ammonium hydroxide solution, instead of lime slurry, as the regenerant for the anion exchange resin. This improvement is clearly demonstrated in Table 3 and Table 4. Table 3 shows the best set of experimental results obtained during the H_2SO_4-NH_4OH operation series, while Table 4 is the summary of a one month period steady-state operation under the identical operation conditions which have been given in Section 5. This one month period, which will be discussed later, occurred near the end of the entire study. It was characterized by a minimum of mechanical problems.

As indicated in Table 3, the concentration of the ammonium ion was increased in the anion column effluent, thus reducing the removal efficiency from 88 percent as achieved by the cation exchange column alone to 69 percent. This adverse effect on the ammonium ion removal by the anion exchange resin could be attributed to the inadequate rinsing operation in the anion column. Several other operating conditions, within the limitations of the existing pilot plant, were tried to improve the rinsing operation, however, all those alternatives failed to show any improvement without deteriorating the overall removal of the anions. As shown in Table 4, the ammonium ion removal during one month of steady-state operation period was only 41 percent compared to 69 percent removal during the best run. This might have been complicated by the problems associated with the resin putsing operation.

REGENERATION EFFICIENCIES

During the steady-state operation period, the average product flow rate was about 34 lpm (9 gpm). Based on this average flow rate and the average ion concentrations as shown in Table 4, the chemical loadings for the cation and anion exchange resins per minute of the run cycle were estimated to be 340 milliequivalents and 190 milliequivalents, respectively. The bicarbonate ion was not included in the estimate for the anion exchange resin. In order to maximize the regenerant utilization, only equivalent rates of sulfuric acid and ammonium hydroxide dosages were applied to the respective regeneration sections to match the chemical loadings.

TABLE 7. PILOT PLANT TEST PERFORMANCE USING H_2SO_4-NH_4OH REGENERATION MODE

Parameter		Carbon Column Effluent (Feed)	Cation Column Effluent	Anion Column Effluent (Product)	Removal %
Calcium	mg/l	47	0.10	0.05	100
Magnesium	mg/l	14	0.02	0.04	100
Sodium	mg/l	106	1.2	0.80	99
Potassium	mg/l	11	1.0	1.0	92
Ammonium (NH_4-N)	mg/l	16	2.2	4.9	69
Sulfate	mg/l	103	103	1.2	99
Chloride	mg/l	100	100	20	80
Nitrate (NO_3-N)	mg/l	0.30	0.32	0.04	87
Phosphate (PO_4)	mg/l	17	17	0.55	97
Total Alkalinity ($CaCO_3$)	mg/l	220		6	
Acidity ($CaCO_3$)	mg/l		224		
Total Dissolved Solids	mg/l	525	173	46	91
pH		7.4	2.5	5.4	
Conductivity	$\mu mhos/cm$	970	1660	60	94
Chemical Oxygen Demand	mg/l	5.8	5.8	0.20	97

TABLE 4. AVERAGE WATER CHARACTERISTICS DURING STEADY-STATE PILOT PLANT OPERATION

(H,SO,-NH,OH REGENERATION MODE)

Parameter			Carbon Column Effluent (Feed)	Cation Column Effluent	Anion Column Effluent (Product)	Removal %
Calcium		mg/l	47	1.2	1.3	97
Magnesium		mg/l	7.4	0.42	0.38	97
Sodium		mg/l	106	13	13	89
Potassium		mg/l	12	3.0	3.0	75
Ammonium	(NH_4-N)	mg/l	22	6.7	13	41
Sulfate		mg/l	108	134	2.8	98
Chloride		mg/l	91	92	31	66
Nitrate	(NO_3-N)	mg/l	0.88	0.31	0.13	85
Phosphate	(PO_4)	mg/l	20	19	0.74	96
Total Alkalinity	($CaCO_3$)	mg/l	256		49	81
Acidity	($CaCO_3$)	mg/l		203		
Total Dissolved Solids		mg/l	511	217	90	82
pH			7.3	2.6	5.0	
Conductivity		mMhos/cm	1030	1700	196	81

Under such stoichiometric regenerant feed rate for both cation and anion exchange resins, the average removal rates by the respective resins were found to be about 300 milliequivalents per minute for cations and 170 milliequivalents per minute for anions. Therefore, the regeneration efficiencies as calculated by the following equation were about 88 percent and 90 percent for the cation and anion exchange resins, respectively.

$$\text{Regeneration Efficiency (\%)} = \frac{\text{total equivalents of ions removed}}{\text{total equivalents of regenerant applied}} \times 100$$

The regeneration efficiencies achieved by this study were slightly higher than those of the two-stage fixed-bed ion exchange process (2). However, the average TiO_2 removal demonstrated by this pilot plant operation was only about 82 percent, which was lower than the 88 percent achieved by the two-stage fixed-bed ion exchange process at similar regenerant dosage level. Furthermore, the regeneration efficiencies of this pilot plant study were not as consistent as those from the fixed-bed system on a day-to-day basis.

During this regeneration operation, the most serious problem was the plugging of the waste collector screen and the waste discharge line of the cation exchange column. The plugging problem was minimized by replacing the waste collector screen once every two to three weeks.

BRINE CHARACTERISTICS

In this continuous counter-current ion exchange pilot plant study, the rinse water and the spent regenerant were combined into the same brine stream in each regeneration vessel. Therefore, the brine flow rate for the cation and anion exchange columns could be measured separately in each corresponding brine holding tank. The average rate of brine flow for the cation column was about 98 liters (26 gallons) per hour, while the average rate for the anion column was about 72 liters (19 gallons) per hour. All these rates were measured during the 9:50-4a.00 steady-state operation period. The brine/product ratio for each brine stream was estimated to be 4.8 percent and 3.5 percent for the cation and anion columns, respectively. Thus, the combined brine/product ratio for the continuous counter-current system operation was approximately 8.3 percent which was slightly lower than the 11 percent required by the two-stage fixed-bed ion exchange process. However, when lime slurry was used instead of ammonium hydroxide, the brine/product ratio for the anion column alone was found to be as high as 12 percent.

Table 5 shows the average results of the chemical analyses of the brine samples taken during the H_2SO_4-NH_4OH steady-state operation period. The strength of the brine produced in this series of operations was practically equal to the two-stage fixed-bed operation.

RESIN STABILITY

Before the initiation of the series of intensive pilot plant operations on March 1, 1972, some resin samples from both ion exchange columns were taken for screen analysis of the resin particle size distributions. The typical results of these analyses are presented in Table 6 for both cation and anion exchange resins. The same type of analysis was applied to the resin samples taken after the termination of the entire pilot plant operations, and the typical results are also included in Table 6. As indicated in this table, the particle size distributions for both cation and anion exchange resins had been significantly shifted toward smaller sizes as a result of the intensive plant operations. However, most of the resin particles examined under magnifier were still in perfect whole bead condition after the entire series of operations.

Some screen analyses had also been performed on the resin samples taken from the resin recovery tanks. The typical results are shown in Table 7. The anion resin recovery tank seemed to have more fine resin particles as indicated in Table 7. However, it was found that fewer of the anion exchange resin beads were chipped by attrition than the cation exchange resins. About three percent of the cation resin beads in the resin recovery tank were chipped.

A complete survey of the resin inventory in each ion exchange column was made before the start of the intensive operation schedule on March 1, 1972, and the same survey was conducted again on August 31, 1972 after the termination of the pilot plant study. During this period, a total of 2760 hours of onstream operations were conducted with the pilot plant. The results of the resin inventory survey indicated that about 1.5 percent of cation resins and 4.5 percent of anion resins were lost during the 2760 hours of operations. Most of the resin losses might be attributed to the attrition effects of the various valve operations along the loop path of the resin flow. The resin fines thus produced were then stripped out of the column by the backwash water.

During the pilot plant operations, no permanent impairment of the resin operational exchange capacity was detected. Therefore, it appears quite conservative to assume an annual 10 percent replacement for cation resin and 20 percent for anion resin in the process cost estimate.

TABLE 5. AVERAGE BRINE CHARACTERISTICS DURING STEADY-STATE PILOT PLANT OPERATION (H_2SO_4-NH_4OH REGENERATON MODE)

Parameter			Cation Column Brine	Anion Column Brine
Calcium		mg/l	1,000	26
Magnesium		mg/l	258	8.3
Sodium		mg/l	1,970	54
Potassium		mg/l	185	6.0
Ammonium	(NH_4-N)	mg/l	302	2,030
Sulfate		mg/l	9,290	4,450
Chloride		mg/l	62	2,110
Nitrate	(NO_3-N)	mg/l	0.32	3.9
Orthophosphate	(PO_4)	mg/l	8.6	344
Total Alkalinity	($CaCO_3$)	mg/l		2,930
Acidity	($CaCO_3$)	mg/l	570	
Total Dissolved Solids		mg/l	11,700	7,240
pH			3.4	7.6
Conductivity		umhos/cm	11,400	19,000

TABLE 6. TYPICAL SCREEN ANALYSIS OF RESIN PARTICLE SIZE DISTRIBUTION

U.S. Standard Sieve Number	Resin From Cation Column (Percent Retained on Sieve)		Resin From Anion Column (Percent Retained on Sieve)	
	Before Study	After Study	Before Study	After Study
20	32	23	14	8
30	46	52	52	40
40	17	20	25	32
60	2	1	7	10
80	2	1	1	7

TABLE 7. PARTICLE SIZE DISTRIBUTIONS OF THE RESINS FROM RESIN RECOVERY TANKS

U.S. Standard Sieve Number	Cation Resin (% Retained on Sieve)	Anion Resin (% Retained on Sieve)
20	14	3
30	41	15
40	32	35
60	10	32
80	1	10

PROCESS RELIABILITY

The performance of the Chem-Seps ion exchange pilot plant, as illustrated in Figure 5, was very inconsistent on a day-to-day basis. Most of the problems encountered during the pilot plant operations were mechanical in nature. The inaccuracy of the resin pulsing control caused most serious damage to the process performance. Other mechanical problems as listed below could also be responsible for the inconsistency of the process performance.

A. The conductivity control mechanism in the rinse section was not sensitive enough;

B. The collector screen in cation regeneration section was frequently plugged;

C. The sequence for the applications of the regenerants and the rinse water was not efficiently programmed; and

D. The feed pressure of the pulsing water might not be high enough.

If all the above problems could be properly adjusted and corrected, the performance of the continuous counter-current ion exchange pilot plant would be more reliable and satisfactory.

During the last month of the pilot plant operation, the plant was able to function steadily with relatively fewer mechanical problems. The performance results of this one-month period steady-state operations are shown in Figure 5 and Table 4. Most of the process evaluations and the process cost estimates have been based on the data collected during this relatively trouble free steady-state operation period.

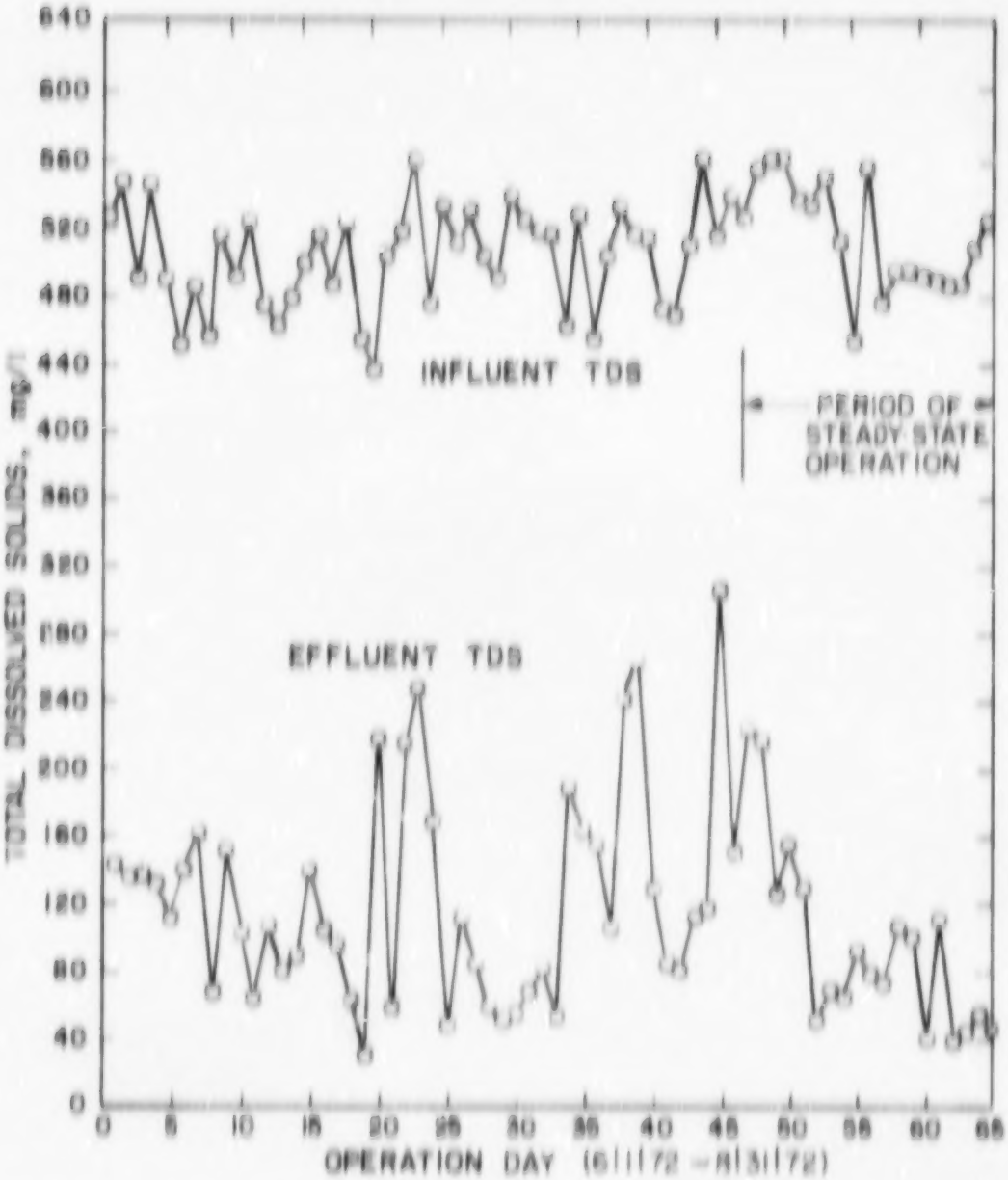


Figure 5. Performance of the CHEM-SEP'S continuous counter-current ion exchange system.

SECTION 7

PROCESS COST ESTIMATE

A preliminary cost estimate, based on the Pomona pilot plant operations, has been prepared for a 37,850 cu m/day (10 MGD) continuous counter-current ion exchange plant for wastewater demineralization. The itemized cost estimates as well as the assumptions used for making the cost estimates are shown together in Table 8. As indicated in Table 8, the total process cost (excluding the costs for carbon adsorption pretreatment and brine disposal) for achieving an 82 percent demineralization is about 4.9¢/1,000 liters (18.5¢/1,000 gallons). This cost will be increased to 7.4¢/1,000 liters (28.1¢/1,000 gallons) if the carbon pretreatment cost is included.

In most wastewater reuse applications, it may require the removal of an amount equivalent to that added during one domestic use of the water, instead of requiring the removal of 82 percent of the influent TDS as achieved by the Chem-Seps pilot plant operation. In most cases, the amount added during one domestic use of the water is about 300 mg/l TDS. This is about one-half of the influent TDS in Pomona wastewater. Therefore, it is reasonable assumption that about one-half of influent TDS will require removal in wastewater demineralization. It is presently envisioned that product water of this quality, with one-half TDS reduction, will be achieved by blending the highly demineralized ion exchange product water with wastewater which has been treated by carbon adsorption but has not been demineralized. The total process cost of such a blended product water in a complete recycle system is estimated to be about 5.2¢/1,000 liters (20.1¢/1,000 gallons), which includes the cost for carbon adsorption pretreatment but not the brine disposal cost. This estimate has assumed a capacity of 37,850 cu m/day (10 MGD) for ion exchange portion of the overall process. Since only about 60 percent of the total flow must be demineralized with 82 percent TDS reduction, the corresponding total blended flow is about 63,210 cu m/day (16.7 MGD). Should the total blended flow be less, the ion exchange plant would be correspondingly smaller and the unit cost would be increased somewhat.

If the final TDS of a blended product water in a complete recycle system is acceptable at the level of 500 mg/l, then the

TABLE 8. PROCESS COST ESTIMATE

Plant size = 37,850 cu m/day (day MGD)

	¢/1,000 liters	¢/1,000 gallons
Capital		
$1,200,000	0.8	2.9
Operation and Maintenance		
Regeneration Chemicals		
Sulfuric Acid	2.2	8.3
Ammonium Hydroxide	0.9	3.5
Resin Replacement	0.2	0.7
Power	0.3	1.0
Labor	0.3	1.3
Maintenance Materials	0.2	0.8
Total Process Cost	4.9	18.5

Assumptions:-

1. Influent TDS = 600 mg/l; TDS Removal = 82%.
2. Regeneration Efficiencies: Cation = 88%; Anion = 90%.
3. Resin Replacement: Cation = 10%/year; Anion = 20%/year.
4. Sulfuric Acid = $36/ton; Ammonium Hydroxide = $80/ton.
5. Resin Costs: Cation = $1/l; Anion = $2/l.
6. Power = 1¢/kwh.
7. Labor = 4 at $9,600/year.
8. Costs for carbon pretreatment (2.5¢/1,000 liters) and brine disposal are not included in the estimate.
9. The capital cost is amortized for 20 years at 6% interest.
10. The estimate is based on August, 1973 material and construction costs.

total process cost can be reduced to 4.7¢/1,000 liters (18.1¢/1,000 gallons), including the cost for carbon adsorption pretreatment but not the brine disposal.

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APPENDIX A

ANALYTICAL PROCEDURES FOR DETERMINING THE RESIN CAPACITY (5)

The weak base anion resin capacity, loaded (LR) or stripped (SR), is determined by feeding an excess of a known amount of standardized acid. The OH-form resin capacity (as meq/ml or eq/l) is then obtained by dividing the acid sorbed (meq) by the resin used (ml).

Example:

1. 25 ml of resin is used in a column.
2. 150 ml of 0.5 N acid is fed to the column. This is equivalent to 75 meq.
3. Rinse the column with 3 to 5 bed volumes of distilled water.
4. Measure the volume of rinsed water and titrate the acidity. Assuming 50 meq acidity is titrated.
5. The acid sorbed is then equal to 25 meq (75 meq minus 50 meq).
6. The OH-form capacity is thus equal to 1 eq/l or 1 meq/ml (25 meq/25 ml).

The same technique may be used to measure the H-form capacity of strong acid type resin using standardized base. However, it may not be used for weak acid type resin because the resin capacity is a function of pH. The capacity at pH 13 to 14, when using NaOH, would not be the same as that for water at pH 7.

The other common method is to strip off all cations using about 10 bed volumes of 4 N HCl or HNO_3 and analyzing for all the cations removed.

Example:

1. 25 ml of cation resin is used in a column.
2. 250 ml of 4 N HNO_3 strip solution is applied.
3. Results of cation analyses:

Ca^{++} = 1200 mg/l = 1.2 g/l
Mg^{++} = 400 mg/l = 0.4 g/l
Na^{+} = 800 mg/l = 0.8 g/l

K^+ = 100 mg/l = 0.1 g/l
NH_4^+ = 200 mg/l = 0.2 g/l

4. Total equivalents of cations:

Ca^{++} = 1.2/20 x 250/25 = 0.60 (eq/l)
Mg^{++} = 0.4/12 x 250/25 = 0.33 (eq/l)
Na^+ = 0.8/23 x 250/25 = 0.35 (eq/l)
K^+ = 0.1/39 x 250/25 = 0.03 (eq/l)
NH_4^+ = 0.2/18 x 250/25 = 0.11 (eq/l)

Total cations = 1.42 (eq/l)

APPENDIX B

ANALYTICAL PROCEDURES FOR DETERMINING THE TOTAL SALTS (6)

If a sample has a mixture of salts in acid, the free acid is titrated first. Then the sample is run through a bed of H-form resin and titrated again. Subtraction of the free acid gives a measure of the total salts. If a sample is alkaline, then the free base is titrated. When running through a bed of H-form resin the free base is sorbed to form water and salts converted to acid.

$$\left.\begin{matrix} CaSO_4 \\ MgCl_2 \\ NaNO_3 \\ H_2SO_4 \end{matrix}\right\} + HR \rightarrow \begin{matrix} CaR \\ MgR \\ NaR \\ HR \end{matrix} + \begin{matrix} H_2SO_4 \\ HCl \\ HNO_3 \\ \text{plus free } H_2SO_4 \end{matrix}$$

$$\left.\begin{matrix} CaSO_4 \\ MgCl_2 \\ NaNO_3 \\ NaOH \end{matrix}\right\} + HR \rightarrow \begin{matrix} CaR \\ MgR \\ NaR \\ HR \end{matrix} + \begin{matrix} H_2SO_4 \\ HCl \\ HNO_3 \end{matrix}$$

Recommended sample size is as follows:

1	-	10	meq/l	100 ml
10	-	100	"	10 ml
100	-	2000	"	1 ml
2000	-	10,000	"	0.1 ml

Any laboratory sized column of resin may be used; commonly 25 ml to 100 ml. Standard 20-50 mesh resin is satisfactory, but 50-100 mesh is preferred because its flow rate is self-moderating. Also, because of the smaller resin size, the exchange zone is sharper. It is important that the

exchange capacity of the resin is never exceeded. Usually it is regenerated after 1/2 to 2/3 of the capacity is used up. Relative to technique it is important that all the acid produced from each sample is completely rinsed out of the bed. This is commonly checked with pH paper. After familiarity one will find that 3 to 5 bed volumes of rinse is adequate.

After exhaustion, the bed must be quite thoroughly regenerated. This may be done by using 10 bed volumes of 4 M HCl or HNO_3. Remember to rinse out all free acid. The resin shrinks a little on treatment with strong solutions. It is helpful to fluff up the bed and let it resettle before the final rinse. Never do this between regeneration because it is necessary that all loaded resin be on top and the bottom of the bed always 100 percent H-form.